

Gradient-dependent upper bound for the exchange-correlation energy and application to density functional theory

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We propose a simple gradient-dependent bound for the exchange-correlation energy (sLL), based on the recent non-local bound derived by Lewin and Lieb. We show that sLL is equivalent to the original Lieb-Oxford bound in rapidly-varying density cases but it is tighter for slowly-varying density systems. To show the utility of the sLL bound we apply it to the construction of simple semilocal and non-local exchange and correlation functionals. In both cases improved results, with respect to the use of Lieb-Oxford bound, are obtained showing the power of the sLL bound.

The Lieb-Oxford (LO) bound¹, $E_{xc}[n_\lambda] \geq LO[n_\lambda]$ with $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda\mathbf{r})$ being the uniformly scaled density and

$$LO[n_\lambda] = -1.68 \int n_\lambda^{4/3}(\mathbf{r}) d\mathbf{r}, \quad (1)$$

is one of the main exact constraints for the exchange-correlation (XC) energy and is used in the construction of many semilocal XC approximations^{2–11}. Several works have concerned the tightening of this bound. Chan and Handy¹² proposed to reduce the constant in LO to 1.6358. Odashima and Capelle¹³ used numerical analysis to further reduce it to 1.444. Conversely, considering the low-density limit of the spin-unpolarized uniform electron gas, it is found that the constant cannot be smaller than 1.437¹⁴. Consequently the value 1.4 has been employed to build some recent XC functionals^{15–17}.

Very recently Lewin and Lieb¹⁸ derived a different bound, having a density dependence, i.e. $E_{xc}[n_\lambda] \geq LL[n_\lambda]$ where

$$LL[n_\lambda] = -1.451 \int n_\lambda^{4/3}(\mathbf{r}) d\mathbf{r} - 0.327 \left[\int |\nabla n_\lambda| d\mathbf{r} \right]^{1/4} \left[\int n_\lambda^{4/3} d\mathbf{r} \right]^{3/4}. \quad (2)$$

Note that both the LO and LL bounds scale as the exchange energy under a uniform scaling of the density. However, the LL bound, in the present form, is not very practical for development in density functional theory. Thus, in this communication we consider a simplified form for such a bound which, at the same time, tightens it, such as to provide a useful tool for XC functional development.

To start we note that the LL bound is tighter than the LO one only for slowly-varying densities, where $|\nabla n_\lambda|$ is small. Let first consider the XC energy in this regime (spin-unpolarized case), in the low-density limit ($\lambda \rightarrow 0$), where the second-order gradient expansion of the XC

energy¹⁹ becomes exact

$$\begin{aligned} E_{xc}[n_\lambda] &= -1.437 \int n_\lambda^{4/3} d\mathbf{r} - 0.091 \int n_\lambda^{4/3} s^2 d\mathbf{r} \\ &+ \int n_\lambda \beta t_\lambda^2 d\mathbf{r} \geq \\ &\geq -1.437 \int n_\lambda^{4/3} d\mathbf{r} - 0.091 \int n_\lambda^{4/3} s^2 d\mathbf{r} \geq \\ &\geq -1.451 \int n_\lambda^{4/3} d\mathbf{r} - 0.091 \int n_\lambda^{4/3} s^\alpha d\mathbf{r}, \quad (3) \end{aligned}$$

for any $\alpha \leq 2$, and where $s = |\nabla n_\lambda|/[2(3\pi^2)^{1/3} n_\lambda^{4/3}]$ and $t_\lambda = |\nabla n_\lambda|/[2(3/\pi)^{1/6} n_\lambda^{7/6}]$ are the reduced gradients for exchange and correlation respectively (note that s is invariant under the uniform scaling while $t_\lambda \propto \lambda^{1/2}$) and $\beta \geq 0$ is the second order expansion coefficient for correlation. Note that β is known only in the high-density limit, and in the metallic range¹⁹ (i.e. $2 \leq r_s \leq 6$, with $r_s = [3/(4\pi n)]^{1/3}$ being the bulk parameter). The last inequality uses the fact that $s \leq 1$ in the considered limit. Eq. (4) suggests that in the low-density limit a gradient-dependent term may play an important role to the bound, similar with the LL expression.

On the other hand, starting from the LL bound and using the Hölder inequality we find

$$E_{xc}[n_\lambda] \geq -1.451 \int n_\lambda^{4/3} d\mathbf{r} - 0.516 \int n_\lambda^{4/3} s^{1/4} d\mathbf{r}. \quad (5)$$

This provides a slightly tighter bound than LL (not mathematically rigorous but in the spirit of Ref. 13, as explained below), and it can be used together with Eq. (4) to obtain a more useful formula for the bound.

In fact, a comparison of Eqs. (4) and (5) suggests that the correct bound could be

$$sLL[n_\lambda] = -1.451 \int n_\lambda^{4/3} d\mathbf{r} - C \int n_\lambda^{4/3} s^{1/4} d\mathbf{r}, \quad (6)$$

with $0.09 \leq C \leq 0.52$ (to be fixed later). A similar idea is also proposed in Ref. 20. This ansatz is also

supported by a further analysis of the XC energy under the uniform scaling to the low-density limit at any value of s (note that instead Eq. (4) holds only for $s < 1$). To see this, consider the partitioning the XC energy as $E_{xc}[n_\lambda] = E_{xc}^{LDA}[n_\lambda] + E_{xc}^{GE2}[n_\lambda] + \delta E_x[n_\lambda] + \delta E_c[n_\lambda]$, where LDA denotes the local density approximation, $GE2$ denotes the second-order gradient expansion terms, and δE_x and δE_c indicate higher-order exchange and correlation contributions. Because in this limit $t \rightarrow 0$ we can set $\delta E_c \approx 0$. Moreover, following Ref. 8, we can assume that $E_{xc}^{GE2}[n_\lambda] \approx 0$ for $\lambda \rightarrow 0$. Hence,

$$\begin{aligned} E_{xc} &\approx E_{xc}^{LDA}[n_\lambda] + \delta E_x[n_\lambda] = \\ &= -1.44 \int n_\lambda^{4/3} d\mathbf{r} - C_X \int_{s \geq 1} n_\lambda^{4/3} [f_x^{exact}(s) - 1] d\mathbf{r}, \end{aligned} \quad (7)$$

with $C_x = (3/4)(3/\pi)^{1/3}$ and f_x^{exact} is the exact exchange enhancement factor. Noting that at large gradients $f_x^{exact} - 1 \geq 0$, Eq. (7) shows that a tighter LO bound may fail in the low-density regime (where both LDA correlation and exchange scale similarly, as $\sim 1/r_s$) and an s -dependent term is instead required.

To fix the parameter C , we consider a tough case for the semilocal sLL bound: the beryllium isoelectronic series up to the nuclear charge $Z = 140$. This is in fact a rapidly-varying high-density limit case with strong correlation ($E_c^{LDA} \geq E_c^{exact} \rightarrow -\infty$ for highly charged ions²¹). While the original LO bound gives $LO/E_{xc} \approx 1.9$, the LL bound is much looser, having $LL/E_{xc} \approx 2.3$ (note that all results are practically independent on the nuclear charge). Hence, our constraint is that $sLL \approx LO$ for such a case (that is representative for rapidly-varying density regime). In this way we obtain $C = 0.245$.

The bound of Eq. (6) can be tested for different systems. In case of atoms, ions, molecules, and solids this test is trivial because sLL is slightly looser than the local bound of Odashima and Capelle¹³ which was verified for these cases. Hence, we consider here a few additional possibilities, based on interesting model systems.

For slowly-varying density cases the sLL bound is surely verified in the low-density limit, because $C = 0.245 \geq 0.091$. For other density regimes we consider in Fig. 1 jellium spheres with 40 electrons and bulk parameter included in the interval $1 \leq r_s \leq 20$, as well as two interacting jellium slabs of thickness and separation distance equal to the Fermi wave length (similar results are obtained also for other thicknesses and distances) and $1 \leq r_s \leq 20$. The latter describe several density regimes, ranging from slowly- (for thick and close slabs) to very rapidly-varying ones (thin slabs).

In all cases the exchange energy is computed exactly, whereas the correlation energy is estimated using the JS functional²² (similar results are given also by PBE² and TPSS⁷). The LO, sLL, and LL have been calculated using exact exchange densities. These systems are relevant to understand the significance on the bound of quantum oscillations in ordinary matter. Figure 1 shows that in all cases the sLL bound is respected ($sLL/E_{xc} \geq 1$) and

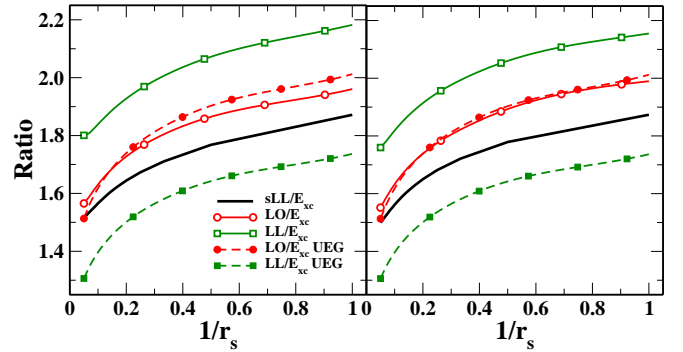


FIG. 1: The ratios LO/E_{xc} , LL/E_{xc} , and sLL/E_{xc} versus $1/r_s$, for $40e^-$ jellium spheres (left panel) and for two interacting jellium slabs (right panel). Also shown are LO/E_{xc} and $LL/E_{xc} = sLL/E_{xc}$, for the uniform electron gas (UEG).

it is tighter than LO. Instead, the non-local LL bound is always rather loose. Finally, comparison with uniform electron gas results shows that quantum oscillations and surface effects have a negligible effect on the LO bound, which does not depend on the gradient, while they give a little weakening of the semilocal sLL bound.

As a different example we consider the one-electron densities

$$n_H(r) = \frac{e^{-2r}}{\pi} \quad ; \quad n_G(r) = \frac{e^{-r^2}}{\pi^{3/2}}. \quad (8)$$

These are models for rapidly-varying density systems and have been shown to be relevant for bonding properties of molecules²³. The calculations are analytical and we readily find: $LO/E_{xc} = 1.55$, $LL/E_{xc} = 1.82$, and $sLL/E_{xc} = 1.56$ for H; $LO/E_{xc} = 1.54$, $LL/E_{xc} = 1.80$, and $sLL/E_{xc} = 1.54$ for G. Thus, the LO and sLL bounds have the same quality, both outperforming the LL bound. The coincidence of LO and sLL for these model systems is reminiscent of the fact that, to fix C in Eq. (6), we constrained sLL to reproduce LO for the Be series, which presents rapidly-varying densities. However, notably in the present case there is no contribution from correlation.

To conclude our analysis we consider finally the opposite case of slowly-varying strong-correlated systems. One example of such systems is given by the point-charge-plus-continuum (PC) model^{24,25}. At small reduced gradients $s \leq 1$, the XC energy is²⁵⁻²⁷

$$E_{xc}^{PC}[n] = -1.451 \int n^{4/3} d\mathbf{r} + 0.203 \int n^{4/3} s^2 d\mathbf{r}. \quad (9)$$

We observe that the local term is exactly the one entering in the LL and sLL bounds and is very close to the numerical estimation of Odashima and Capelle¹³, although this latter bound is formally broken for $s \rightarrow 0$. This shows that this model is the true limit for constant densities. On the other hand, because the second-order XC contribution is positive, all the examined bounds are valid for the PC model for $0 < s \leq 1$.

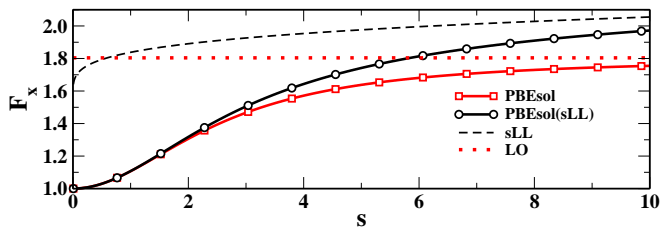


FIG. 2: Exchange enhancement factors versus s , for PBEsol and PBEsol(sLL). Also shown, are the asymptotes of sLL and LO bounds.

Another interesting example of slowly-varying strongly correlated system can be obtained by considering the strong-correlation scaling of the density²⁸, $n_\lambda(\mathbf{r}) = \lambda^{-2}n(\lambda^{-1}\mathbf{r})$, in the limit $\lambda \rightarrow \infty$. Under this scaling the reduced gradients behave as $s_\lambda(\mathbf{r}) = \lambda^{-1/3}s(\lambda^{-1}\mathbf{r})$ and $t_\lambda(\mathbf{r}) = \lambda^{-2/3}t(\lambda^{-1}\mathbf{r})$. The XC energy is dominated by the local terms, while the second-order contributions decay as $\lambda^{-1/3}$. On the other hand, we have $sLL = -1.451\lambda^{1/3} \int n^{4/3}d\mathbf{r} - 0.245\lambda^{1/4} \int n^{4/3}s^{1/4}d\mathbf{r}$. Therefore, for $\lambda \rightarrow \infty$ sLL provides a good bound to the XC energy (note that the local part of sLL is almost the exact limit for the local XC energy). Moreover, we note that in this limit $sLL \leq LO$, being a tighter bound for the XC energy of slowly-varying strongly-correlated systems.

To show examples of the practical utility of the sLL bound we consider its application in the construction of a GGA and an hyper-GGA functional.

GGA. We consider the new sLL bound in the PBEsol³ XC functional, which is a non-empirical GGA with the correct second-order exchange coefficient. The value of $\kappa = 0.804$ in the exchange enhancement factor $F_x = 1 + \kappa - \kappa/[1 + (\mu/\kappa)s^2]$ is replaced by

$$\kappa = 0.559 + 0.279s^{1/4}. \quad (10)$$

in order to respect the sLL bound at any point of the space. For the correlation part we use $\beta = 0.045$ (note that in PBEsol $\beta = 0.046$) refitting jellium surfaces.³ In Fig. 2, we show a comparison of the exchange enhancement factors. Note that any exchange functional that recovers the local LO bound (e.g. PBEsol, TPSS meta-GGA⁷), satisfies also the local sLL bound. Instead, PBEsol with the sLL bound clearly violates the local LO bound.

To test the effect of the sLL bound we performed different tests for solids and molecules. In Table I we report the mean absolute errors (MAEs) for solid-state tests on 24 bulk solids (see computational details). We see that using the sLL bound improves the results: lattice constants and cohesive energies are improved with respect PBEsol, while bulk moduli are almost comparable. We recall that PBEsol is one of the most used semilocal functionals in solid-state physics and, one of the best for lattice constants and bulk moduli²⁹. AM05³⁰ performs slightly worse than PBEsol²⁹ (MAEs on this test sets are 32 mÅ and 8.6 GPa, respectively). A PBEsol functional

TABLE I: Mean absolute error (MAE) for the lattice constants (mÅ), bulk moduli (GPa), and cohesive energies (eV/atom) as obtained from the PBEsol functional with the original LO bound, and with the new sLL bound, for various types of solids. Reference data from Ref. 29.

	PBEsol	
	LO	sLL
Lattice constants (mÅ)		
simple metals	37.6	31.8
transition metals	24.9	23.2
semiconductors	29.6	31.8
ionic solids	20.4	22.2
insulators	6.5	6.3
total MAE	24.5	23.8
bulk moduli (GPa)		
simple metals	1.0	0.9
transition metals	18.7	18.5
semiconductors	7.8	8.1
ionic solids	4.1	5.0
insulators	6.7	6.7
total MAE	7.7	7.9
cohesive energies (eV)		
simple metals	0.15	0.13
transition metals	0.71	0.64
semiconductors	0.31	0.26
ionic solids	0.10	0.06
insulators	0.65	0.60
total MAE	0.37	0.33

with $\kappa = 0.559$ is definitely worse^{31,32}, having MAEs of 35 mÅ, 8.1 GPa and 0.51 eV/atom. This shows the importance of the non-local term of the sLL bound.

In Table II we report the MAEs for several tests on molecular properties that are relevant for semilocal functionals. In this case PBEsol with the new sLL bound is better than PBEsol for all tests (the only exception is the OMRE test) with an overall relative MAE of 0.94. The improvement traces back to the larger non-locality of the sLL bound with respect to the LO one, which provides a better description when large reduced gradients are involved³²⁻³⁴. Note that a further improvement for molecular properties can be obtained by replacing the PBEsol correlation with the zPBEsol one^{23,35}, which is not modifying the sLL bound behavior but improves most of the energetic properties³⁶.

Hyper-GGA. We consider the hyper-GGA correlation functional¹⁷

$$E_c[n] = \int \frac{e_c^{TPSS}(\mathbf{r})}{X(\mathbf{r}) - e_x^{TPSS}(\mathbf{r})} (X(\mathbf{r}) - e_x(\mathbf{r})) d\mathbf{r}, \quad (11)$$

where e_c^{TPSS} and e_x^{TPSS} are the TPSS correlation and exchange energy densities⁷ respectively, $e_x(\mathbf{r})$ is the ex-

TABLE II: Mean absolute errors (MAE) in kcal/mol for energy tests, and in mÅ for geometry tests, for several molecules benchmark, as obtained from the PBEsol functional with the original LO bound, and with the new sLL bound.

test	PBEsol	
	LO	sLL
atomiz. energy (AE6)	34.5	32.1
atomiz. energy (W4)	21.4	20.0
atomiz. energy (W4-MR)	35.5	33.9
3d-metals AE (TM10AE)	18.3	17.6
Au clusters AE (AUnAE)	3.6	3.1
reaction ener. (OMRE)	8.1	10.7
reaction ener. (BH76RC)	6.3	6.0
barrier heights (BH76)	12.2	11.8
3d-metals RE (TMRE)	9.9	9.1
ionization pot. (IP13)	2.3	2.1
proton aff. (PA12)	1.5	1.5
difficult cases (DC9/12)	82.9	78.3
isomerization ener. (ISOL6)	1.7	1.7
interfaces (SI12)	3.8	3.5
hydrogen bonds (HB6)	1.6	1.2
dihydrogen bonds (DHB23)	1.8	1.5
dipole-dipole (DI6)	1.0	0.7
bond lengths (MGBL19)	10.0	9.9
total energy (AE17)	250.3	246.6
$\sum_i \text{MAE}_i / \text{MAE}_i^{\text{PBEsol}}$	1.0	0.94

act exchange energy density (we use only the conventional gauge¹⁷), and $X(\mathbf{r})$ is a local upper bound for the c_x^{TPSS} . We consider two possibilities for this bound: $\int X(\mathbf{r})d\mathbf{r} = \text{LO}$ and $\int X(\mathbf{r})d\mathbf{r} = \text{sLL}$. The corresponding hyper-GGA functionals are labeled hyper(LO) and hyper(sLL). These correlation functionals are exact for one-electron systems, are size-consistent, and even if they are not so realistic¹⁷, they represent very good models to understand local hybrids, and to compare the quality of the LO and sLL bounds. The correlation energies of the atoms from He to Ar as well as of jellium spheres (with 2, 8, 18, 20, 34, 40, 58, 92, and 106 electrons and various r_s), computed with these functionals, are reported in Table III. The hyper(sLL) functional systematically improves over hyper(LO), showing that the sLL bound may be an interesting tool in the construction of non-local functionals.

In conclusion, we showed a new simple gradient-dependent bound (sLL), which has the same quality as the Lieb-Oxford (LO) bound for systems where the density varies rapidly but is significantly tighter for slowly-varying density cases. It is also the exact limit for slowly-varying strongly correlated systems. To indicate the util-

ity of this new bound we applied it to both semilocal and non-local DFT, showing how it can be employed to con-

TABLE III: Mean absolute relative errors (%) for correlation energies of atoms from He to Ar and of magic jellium spheres (js) (average for spheres of 2, 8, 18, 20, 34, 40, 58, 92 and 106 atoms) with different values of r_s . The reference data for jellium spheres are taken from Ref. 37. Accurate atomic correlation energies are taken from Ref. 38.

	PBE	TPSS	hyper(LO)	hyper(sLL)
atoms	6.3	4.9	5.5	5.4
js $r_s = 1$	6.8	6.0	5.6	5.5
js $r_s = 2$	7.9	6.6	6.1	5.9
js $r_s = 3.25$	7.4	5.9	5.4	5.2
js $r_s = 4$	7.1	5.4	5.0	4.8
js $r_s = 5.62$	7.8	5.7	5.4	5.3
Average js	7.4	5.9	5.5	5.3

struct improved exchange and correlation functionals. In particular, we found that the sLL bound improves the accuracy of the PBEsol functional for both solid-state and molecules properties. In addition, we showed that the sLL bound can be fruitfully employed in the construction of hyper-GGAs. Even if the improvements of these functionals are in general small they are rather systematic. This proves the quality of the sLL bound and suggests its importance for development of new functional forms.

Computational details. Equilibrium lattice constants, bulk moduli, and cohesive energies have been calculated for 24 solids, including Al, Ca, K, Li, Na (simple metals); Ag, Cu, Pd, Rh, V (transition metals); LiCl, LiF, MgO, NaCl, NaF (ionic solids); AlN, BN, BP, C (insulators); GaAs, GaP, GaN, Si, SiC (semiconductors). Reference data to construct this set were taken from Ref. 29. These calculations have been performed with the VASP program³⁹ using PBE-PAW pseudopotentials. All Brillouin zone integrations were performed on Γ -centered symmetry-reduced Monkhorst-Pack k -point meshes, using the tetrahedron method with Blöch corrections. For all the calculations a $24 \times 24 \times 24$ k -mesh grid was applied and the plane-wave cutoff was chosen to be 30% larger than maximum cutoff defined for the pseudopotential of each considered atom.

Calculations for Table II have been performed with the TURBOMOLE program package⁴⁰ using a def2-TZVPP basis set^{41,42}. For details about the molecular test sets, see Refs. 43.

Hyper-GGA calculations are non-self-consistent, using accurate exact exchange orbitals and densities.

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